

DECARBOXYLATION OF COAL MODEL COMPOUNDS UNDER LIQUEFACTION CONDITIONS: DOES DECARBOXYLATION LEAD TO RETROGRADE REACTIONS?*

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Introduction

In recent years, it has become clear that oxygen functional groups in low-rank coals are major actors in retrograde reactions which inhibit their efficient thermochemical processing. In the pyrolysis and liquefaction of low-rank coals, low-temperature cross-linking reactions have been correlated with the loss of carboxyl groups and the evolution of CO_2 and H_2O [1,2]. Pretreatments such as methylation, demineralization, or ion-exchange of the inorganic cations reduce cross-linking and CO_2 evolution in pyrolysis [2a,3a]. In pyrolysis and liquefaction, the exchange of Na^+ , K^+ , Ca^{++} , or Ba^{++} into demineralized coal increases cross-linking and CO_2 evolution [3,4]. Cross-linking reactions also have a deleterious effect on liquefaction yields and the distribution of oils, preasphaltenes and asphaltenes [3,4]. These results suggest that decarboxylation may occur by a pathway that initiates retrograde (cross-linking) reactions in the coal polymer independent of the reaction conditions. However, the decarboxylation pathways in liquefaction and pyrolysis of low-rank coals are not known, and it is not clear how decarboxylation leads to cross-linking. Radical recombination or radical addition reactions have been suggested as being involved in retrograde reactions. However, the involvement of radical pathways in thermal decarboxylation reactions has recently been brought into question. We have presented evidence that in the pyrolysis of several bibenzyls containing aromatic carboxylic acids, radical pathways are not involved in thermal decarboxylation reactions and no cross-linking or coupling products are formed [5]. Further, Manion et al. observed that decarboxylation of benzoic acid derivatives in tetralin yielded only small amounts of aryl-aryl coupling products [6]. To gain a better understanding of the role decarboxylation plays in cross-linking reactions during liquefaction in low-rank coals, we have studied the thermal decomposition of several bibenzyls containing aromatic carboxylic acids, and their salts, in the presence of a hydrogen donor solvent (tetralin) and a nondonor solvent (naphthalene). The structures currently under investigation are 1,2-(3,3'-dicarboxyphenyl)ethane (1), 1-(3-carboxyphenyl)-2-(4-biphenyl)ethane (2), and the dipotassium salt of 1,2-(4,4'-dicarboxyphenyl)ethane (3).

Experimental

1,2-(3,3'-dicarboxyphenyl)ethane (1) was synthesized as described previously [5]. The synthesis of 1-(3-carboxyphenyl)-2-(4-biphenyl)ethane (3) and di-potassium 1,2-(4,4'-dicarboxyphenyl)ethane (2) are described below. Tetralin (Aldrich) was purified by washing with concentrated H_2SO_4 until the acid layer was colorless, washing with dilute aqueous NaHCO_3 , followed by fractional distillation under reduced pressure (purity 99.4 % by GC). Naphthalene (Aldrich, 99.9 %) was used without further purification. THF (J.T. Baker HPLC Grade) was distilled from K before use. Gas chromatography analysis was performed using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a J&W Scientific 30 m x 0.25 mm id, 0.25 μm film thickness DB-1 column and a flame ionization detector. Mass spectra were obtained at 70 eV on a Hewlett-Packard 5972 GC/MS equipped with a capillary column identical to that used for GC analysis.

Dipotassium 1,2-(4,4'-dicarboxyphenyl)ethane (3). 1,2-(4,4'-dicarboxyphenyl)ethane [7] (0.498 g, 1.85 mmol) was placed in DMF (10 mL) and aqueous KOH (1.0 M) was added dropwise until the solution became homogeneous. Ethanol (175 mL) was added to precipitate the salt, and the salt was collected by vacuum filtration (0.601 g, 94 %) and dried over P_2O_5 in a vacuum.

Diethyl 3-bromobenzylphosphonate. Into an oven-dried 100 mL flask equipped with a reflux

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condenser was placed 3-bromobenzyl bromide (20.01 g, 80 mmoles) and triethyl phosphite (13.8 mL, 80 mmol). The mixture was heated under argon to 140 °C with stirring for 2 h and then cooled to room temperature. The reflux condenser was replaced with a still head and the mixture was slowly reheated to 170 °C to distill off ethyl bromide and unreacted triethyl phosphite. After cooling, the liquid (24.2 g, 99 %) was stored under argon. GC-MS retention time 17.9 min, m/z (relative intensity) 308 (M^+ , 26), 306 (26), 171 (89), 169 (100), 138 (95).

1-(3-bromophenyl)-2-(4-biphenyl)ethene. Sodium hydride (3.2 g, 60 % mineral oil dispersion, 0.080 moles) was suspended in THF (100 mL) in a 250 mL oven-dried flask under a positive pressure of argon. A solution of diethyl 3-bromobenzylphosphonate (24.5 g, 80 mmol) in THF (100 mL) was transferred to the flask by cannula, and the mixture was stirred for 0.5 h. A solution of 4-biphenylcarboxaldehyde (14.6 g, 80 mmol) in THF (50 mL) was added dropwise over a period of 1 h, and the solution was refluxed for 2 h. The reaction was quenched with H_2O (200 mL) and a white solid was collected by vacuum filtration (19.4 g, 78 %). GC-MS retention time 26 min, m/z (relative intensity) 336 (M^+ , 98), 334 (100), 255 (21).

1-(3-carboxyphenyl)-2-(4-biphenyl)ethene. 1-(3-bromophenyl)-2-(4-biphenyl)ethene (12.0 g, 35.8 mmol) was weighed into an oven-dried flask under an atmosphere of argon and THF (300 mL) was added. The stirred solution was cooled to -78 °C and n -BuLi (14.5 mL, 2.5 M solution in hexane, 35.8 mmol) was added over a period of 0.25 h and the solution was stirred for 0.5 h. Carbon dioxide (produced from warming dry ice and passed through a $CaSO_4$ drying tube) was bubbled through the solution for 1.5 h. The solution was warmed to room temperature and quenched with 10 % H_2SO_4 (100 mL) and H_2O (300 mL). The THF layer was collected and the aqueous layer was extracted with THF (2 x 200 mL). The combined organic layers were washed with H_2O (100 mL) and dried over Na_2SO_4 . The THF was removed under reduced pressure to produce 10.1 g (93 %) of a white solid. GC-MS, analyzed as the trimethyl silyl ester, retention time 27.8 min, m/z (relative intensity) 372 (M^+ , 100), 357 (32), 283 (20).

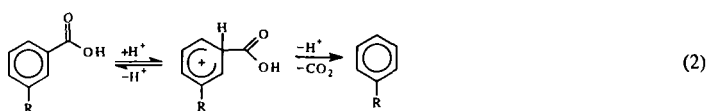
1-(3-carboxyphenyl)-2-(4-biphenyl)ethane (2). Crude 1-(3-carboxyphenyl)-2-(4-biphenyl)ethene (3.02 g, 10.1 mmol), 10 % Pd/C (0.30 g), and EtOH (50 mL) were placed into a Parr hydrogenation bottle and shaken under 50 psi of H_2 until 1-(3-carboxyphenyl)-2-(4-biphenyl)ethene could no longer be detected by GC analysis (72 h). The solution was vacuum filtered and the Pd/C was washed with CH_2Cl_2 . The solution was evaporated to dryness producing a white solid (3.10 g, 99%). GC-MS, analyzed as the trimethylsilyl ester, retention time 25.5 min, m/z (relative intensity) 374 (M^+ , 9), 359 (6), 207 (3), 167 (100). The product was recrystallized 4 times from isopropyl alcohol (GC purity 99.9 %) and dried in vacuum with P_2O_5 prior to use in pyrolysis.

Pyrolyses. Pyrolyses in tetralin were performed by weighing the carboxylic acid and tetralin into a pyrex glass tube. The sample was frozen in liquid N_2 , evacuated (10^{-4} Torr), backfilled with argon, and allowed to warm to room temperature. This process was repeated 7 times, the sample was frozen, the tube was evacuated (ca. 10^{-5} Torr), and sealed. Pyrolyses in naphthalene were performed by loading pyrex tubes with the appropriate amounts of carboxylic acid and naphthalene and conducting 3 freeze-pump-thaw cycles prior to sealing the tube at 10^{-5} Torr. The neat acid was pyrolyzed in sealed pyrex tubes (sealed at ca. 10^{-5} Torr). The pyrolyses were performed in a Tecam fluidized sandbath at 400 ± 1.5 °C. Following the pyrolysis, the samples were quickly removed from the sandbath and cooled in liquid N_2 . The tubes were cracked open, and the solid products were removed with a 2:1 mixture of pyridine: N,O -bis(trimethylsilyl)trifluoroacetamide (BSTFA). Internal standards (2-phenylbenzoic acid and 2,4,6-trimethylbenzoic acid for (1) or 3,5-dimethylbenzoic acid for (2)) were added and the reaction mixtures analyzed by GC and GC-MS. For toluene analysis, the solids from the pyrolysis were extracted with CH_2Cl_2 , internal standards (cumene and those mentioned above) were added, and the sample was analyzed by GC. The CH_2Cl_2 was blown off under argon, and the sample was dissolved in BSTFA:pyridine and reanalyzed. The identities of products from the thermolysis of 1 and 2 were determined by GC-MS analysis and were further confirmed by comparison with commercially available or synthesized authentic materials.

Results and Discussion

Thermolysis of 1 and 2 in Tetralin and Naphthalene

Previously, we have studied the pyrolysis of neat 1 at 400 °C [5]. The major products in the pyrolysis are shown in equation 1, and a typical product distribution for a 30 min pyrolysis is given in Table 1, entry 1. Excellent mass balances were observed in these thermolyses (97 % at 67 % conversion) and no coupling or high molecular weight products were observed by GC or HPLC analysis. From these results, we proposed that decarboxylation occurs by an acid-promoted, ionic mechanism as shown in equation 2. We have now extended our study of thermal decomposition of

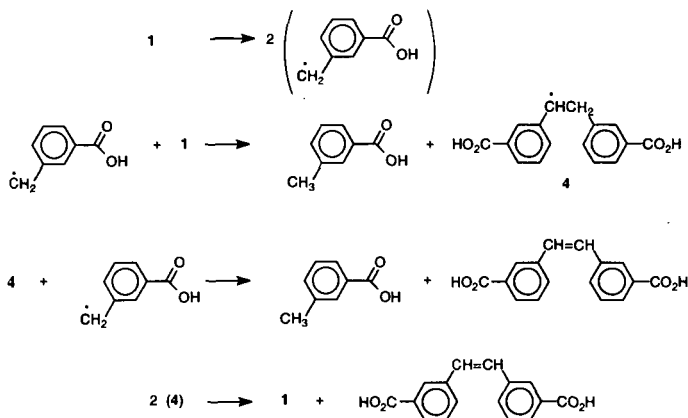


(3)

The results of the thermolysis of 1 and 2 in a hydrogen donor and nondonor solvent at 400 °C show that decarboxylation is a major reaction pathway. Despite the large amount of decarboxylation, no cross-linked products are detected. The good mass balances suggest that decarboxylation does not lead to any significant amounts of undetected coupling or cross-linking products. Compared to the pyrolysis of the neat acids, dilution with either a hydrogen donor solvent or a nondonor solvent increases the mole % of toluene products formed and decreases the amount of decarboxylation. This trend is due to a decrease in the rate of decarboxylation with dilution. The rate of unimolecular C-C homolysis, which leads to the toluene products, is unaffected by dilution. On the basis of the similar effect of dilution by a hydrogen donor and nondonor solvent, we propose that decarboxylation is occurring by an acid-promoted, ionic mechanism (eq 2) under "liquefaction" conditions. The source of acid for this decarboxylation is believed to be a second molecule of carboxylic acid and a second-order process is supported by the observation that the rate of decarboxylation decreases when compounds 1 and 2 are diluted in naphthalene or tetralin. Additional

investigations into the reaction order for decarboxylation are currently in progress. Furthermore, we have established that a substituent effect is present that supports the mechanism in equation 2. The rate of decarboxylation of 1,2-(4,4'-dicarboxyphenyl)ethane (5) is roughly a factor of 2 faster than 1 neat or diluted in diphenyl ether. If the rate-determining step is *ipso*-protonation of the aromatic ring, as shown in equation 2, the *para*-alkyl substituent in 5 would stabilize the carbocation intermediate while the *meta*-alkyl substituent in 1 would not. McMillen has also observed that benzoic acids containing electron donating substituents (-OH and -OMe) decarboxylate faster than benzoic acid at 400 °C in tetralin [6]. This enhanced rate with activated benzoic acids in tetralin provides additional evidence that supports the acid-promoted ionic decarboxylation pathway shown in equation 2.

The results in Tables 1 and 2 also show that in tetralin, the formation of stilbene products is suppressed. The toluic acid and stilbene derivatives are formed by a free-radical reaction analogous to that reported for the thermolysis of bibenzyl [8,9]. Homolysis of 1 produces 2 ($\text{HO}_2\text{CPhCH}_2\cdot$), which can form toluic acid by hydrogen abstraction from tetralin or 1 to form $\text{HO}_2\text{CPhCH}_2\text{CH}(\cdot)\text{PhCO}_2\text{H}$ (4) (Scheme 1, the same pathway will also occur with 2). Because



Scheme 1

tetralin is in large excess (10-fold), it quenches most of the free-radicals and any 4 produced will hydrogen abstract from tetralin before undergoing disproportionation to form stilbene. Also, stilbenes have been shown to react with tetralin at 400 °C to produce bibenzyl [10].

Thermolysis of 3 in Tetralin and Naphthalene

The exchange of inorganic cations, such as Na^+ , K^+ , Ca^{++} , or Ba^{++} , into demineralized low-rank coals can significantly decrease the liquefaction yields. For example, in the liquefaction (400 °C, 30 min, tetralin, H_2) of Zap lignite coal, exchange of potassium cations into an acid demineralized coal increases retrogressive reactions and decreases the liquefaction yields 40 % compared to the demineralized coal [3]. For Wyodak and a North Dakota lignite, ion exchange of potassium cations into the coal decreases the liquefaction yields 25 % compared to an acid demineralized coal [4]. Thermolysis of the dipotassium salt (3) was investigated in tetralin and naphthalene at 400°C for 0.5 h. No products were detected in either solvent and 3 was recovered unreacted (>99 % by GC analysis of the reaction mixtures). In addition, we have found that the neat salts are stable at 400 °C for times up to 2 h. The dipotassium salt is relatively stable at 400 °C under the liquefaction and inert solvent conditions and the salt remained solid during the thermolysis. These preliminary results suggest that the salts of aromatic carboxylic acids do not readily undergo decarboxylation that might lead to cross-linking reactions. Further investigation of the decarboxylation of inorganic salts of carboxylic acids is planned using the carboxy salts of 1 and 2 under liquefaction conditions.

Summary and Conclusion

The thermolysis of two aromatic carboxylic acids 1 and 2 and a dipotassium salt of a carboxylic acid (3) have been investigated at 400 °C as models of carboxylic acids in low rank coals under liquefaction and inert solvent conditions. Thermolysis of acids 1 and 2 leads to a large amount of decarboxylation products, but no evidence for the occurrence of retrograde reactions associated

with the decarboxylation process. It is proposed that the decarboxylation occurs by an acid-promoted, ionic pathway and further investigation of this reaction mechanism under liquefaction conditions is in progress. The dipotassium carboxy salt, 3, is relatively stable at 400 °C and decarboxylation is not observed under liquefaction or inert solvent conditions. This preliminary result suggests that formation of carboxy salts in low-rank coals does not contribute to the retrograde chemistry. Overall, the results of both the acids and salt suggest that decarboxylation does not contribute to retrogressive reactions during the thermal processing of low-rank coals under liquefaction conditions. The evolution of CO₂ from low rank coals during thermal processing may well be coincidental with the chemistry occurring that results in cross-linking.

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Table 1. Product Distributions Observed from the Thermolysis of *m,m*-HO₂CPhCH₂CH₂PhCO₂H Diluted 10:1 (Molar Ratio) with Tetralin or Naphthalene at 400°C for Various Time Intervals.

Entry	1	2	3	4	5	6
Products (mole %) ^a	30 min (neat)	45 min Naph	45 min Tet	90 min Tet	225 min Naph	225 min Tet
PhCH ₃	0 ^a	0 ^a	0 ^a	0 ^a	13.1	12.7
PhCO ₂ H	0.1	0	0	0	0	0
<i>m</i> -CH ₃ PhCO ₂ H	8.4	28.2	42	34	20.2	21.4
<i>m</i> -CH ₃ CH ₂ PhCO ₂ H	1.5	2.3	0	0	1.1	0.3
PhCH ₂ CH ₂ Ph	0.2	0	0	0	3.1	3.5
PhCH=CHPh	0	0	0	0	0.1	0
<i>m</i> -HO ₂ CPhCH ₂ CH ₂ Ph	77.1	62.5	58	66	55.1	59.7
<i>m</i> -HO ₂ CPhCH=CHPh	0.5	0.3	0	0	2.2	0
<i>m,m</i> -HO ₂ CPhCH ₂ PhCO ₂ H	0	0	0	0	0.3	0
<i>m,m</i> -HO ₂ CPhCH(CH ₃)PhCO ₂ H	4.3	0.6	0	0	1.3	1.8
<i>m,m</i> -HO ₂ CPhCH=CHPhCO ₂ H	7.7	5.4	0	0	2.9	0
Conversion ^b	9.6	6.6	5.7	14.1	34.0	35.2
Mass Balance	99.1	97.1	99.4	96.2	95.0	93.0

a-Analysis for toluene not performed.

b-Based on products identified.

Tet=Tetralin; Naph=Naphthalene

Table 2. Product Distributions Observed from the Thermolysis of *m*-HO₂CPhCH₂CH₂Ph-Ph Diluted 10:1 (Molar Ratio) with Tetralin and Naphthalene at 400°C.

Entry	1	2	3
Product (mole %) ^a	60 min Neat	90 min Tet	90 min Naph
PhCH ₃	0 ^a	5.6	1.1
PhCO ₂ H	1.1	0	0
<i>m</i> -CH ₂ PhCO ₂ H	12.9	34.3	28.2
<i>m</i> -CH ₂ CH ₂ PhCO ₂ H	0.6	0	0.76
<i>p</i> -Ph-PhCH ₃	14.6	38.7	30.7
<i>p</i> -Ph-PhCH ₂ CH ₃	4.0	0	0
<i>p</i> -Ph-PhCH(CH ₃)Ph	0.4	0	0.13
<i>p</i> -Ph-PhCH ₂ CH ₂ Ph	42.4	21.3	24.1
<i>p</i> -Ph-PhCH=CHPh	1.8	0	0
<i>p</i> -Ph-PhCH ₂ Ph- <i>m</i> -CO ₂ H	0.78	0	0.40
<i>p</i> -Ph-PhCH(CH ₃)Ph- <i>m</i> -CO ₂ H	5.14	0	3.0
<i>p</i> -Ph-PhCH=CHPh- <i>m</i> -CO ₂ H	16.1	0	11.4
Conversion % ^b	14.4	11.6	14.2
Mass Balance	95.3	103	99.5

a-Toluene analysis not performed.

b-Based on products identified.

Tet=Tetralin; Naph=Naphthalene